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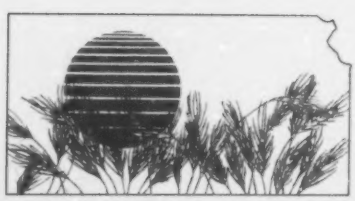
AN EXPERIMENT IN REPRESENTATIVE GROUND-WATER SAMPLING FOR WATER-QUALITY ANALYSIS

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 88-4178

Prepared as part of the
TOXIC-WASTE--GROUND-WATER
CONTAMINATION PROGRAM,
U.S. GEOLOGICAL SURVEY



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By Thomas L. Huntzinger and Lloyd E. Stullken

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Lawrence, Kansas
1988

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CONVERSION FACTORS

For those people who may prefer to use metric (International System) units, the factors for converting the inch-pound units used in this report are given below:

Multiply inch-pound unit	*By*	*To obtain metric unit*
inch	2.54	centimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
acre	4,047	square meter
foot per mile (ft/mi)	0.1894	meter per kilometer
pint (pt)	0.4732	liter
gallon	3.785	liter
pound (lb)	0.4536	kilogram
degree Fahrenheit (°F)	°C = 5/9 (°F -32)	degree Celsius (°C)

Sea level: In this report, sea level refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Mean Sea Level."

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ABSTRACT

Obtaining a sample of ground water that accurately represents the concentration of a chemical constituent in an aquifer is an important aspect of ground-water-quality studies. Varying aquifer and constituent properties may cause chemical constituents to move within selectively separate parts of the aquifer. An experiment was conducted in an agricultural region in south-central Kansas to address questions related to representative sample collection. Concentrations of selected constituents in samples taken from observation wells completed in the upper part of the aquifer were compared to concentrations in samples taken from irrigation wells to determine if there was a significant difference. Water in all wells sampled was a calcium bicarbonate type with more than 200 milligrams per liter hardness and about 200 milligrams per liter alkalinity. Sodium concentrations were also quite large (about 40 milligrams per liter).

There was a significant difference in the nitrite-plus-nitrate concentrations between samples from observation and irrigation wells. The median concentration of nitrite plus nitrate in water from observation wells was 5.7 milligrams per liter compared to 3.4 milligrams per liter in water from irrigation wells. The differences in concentrations of calcium, magnesium, and sodium (larger in water from irrigation wells) were significant at the 78-percent confidence level but not at the 97-percent confidence level. Concentrations of the herbicide, atrazine, were less than the detection limit of 0.1 microgram per liter in all but one well.

INTRODUCTION

Obtaining a sample of ground water that accurately represents the concentration of a chemical constituent in an aquifer is an important aspect of ground-water-quality studies. Varying density, viscosity, and adsorption properties of chemical constituents may cause them to move within selectively separate parts of the aquifer. Chemical and biological processes also may affect concentrations. Therefore, depth within an aquifer may be a significant factor in constituent concentration. Also, constituent concentration within the sample may be affected by integration of the water throughout the interval of the well screen in contact with the aquifer. The potential errors in assuming that samples from full-interval wells represent the average constituent concentration in the aquifer need to be evaluated.

An experiment was conducted in an agricultural region in south-central Kansas (fig. 1) containing large irrigated areas underlain by a shallow water table (30 to 40 ft deep) to address questions related to representative sample collection. A common agricultural practice in the study area is the application of atrazine herbicide for preemergent weed control on corn and the application of nitrogen to maintain optimum soil fertility. Typical procedures to describe the effects of agriculture on ground-water quality would involve the collection of water-quality samples from active irrigation wells, which are screened in various parts of the saturated thickness of the aquifer. Samples from these wells should represent an integration of a substantial part of the aquifer thickness. However, samples taken from water in the upper part of the aquifer potentially contain greater amounts of chemical constituents from the land surface. This report describes the results of an experiment, where concentrations of selected constituents in samples taken from observation wells completed in the upper part of the aquifer were compared to concentrations in samples taken from irrigation wells to determine if there were significant differences.

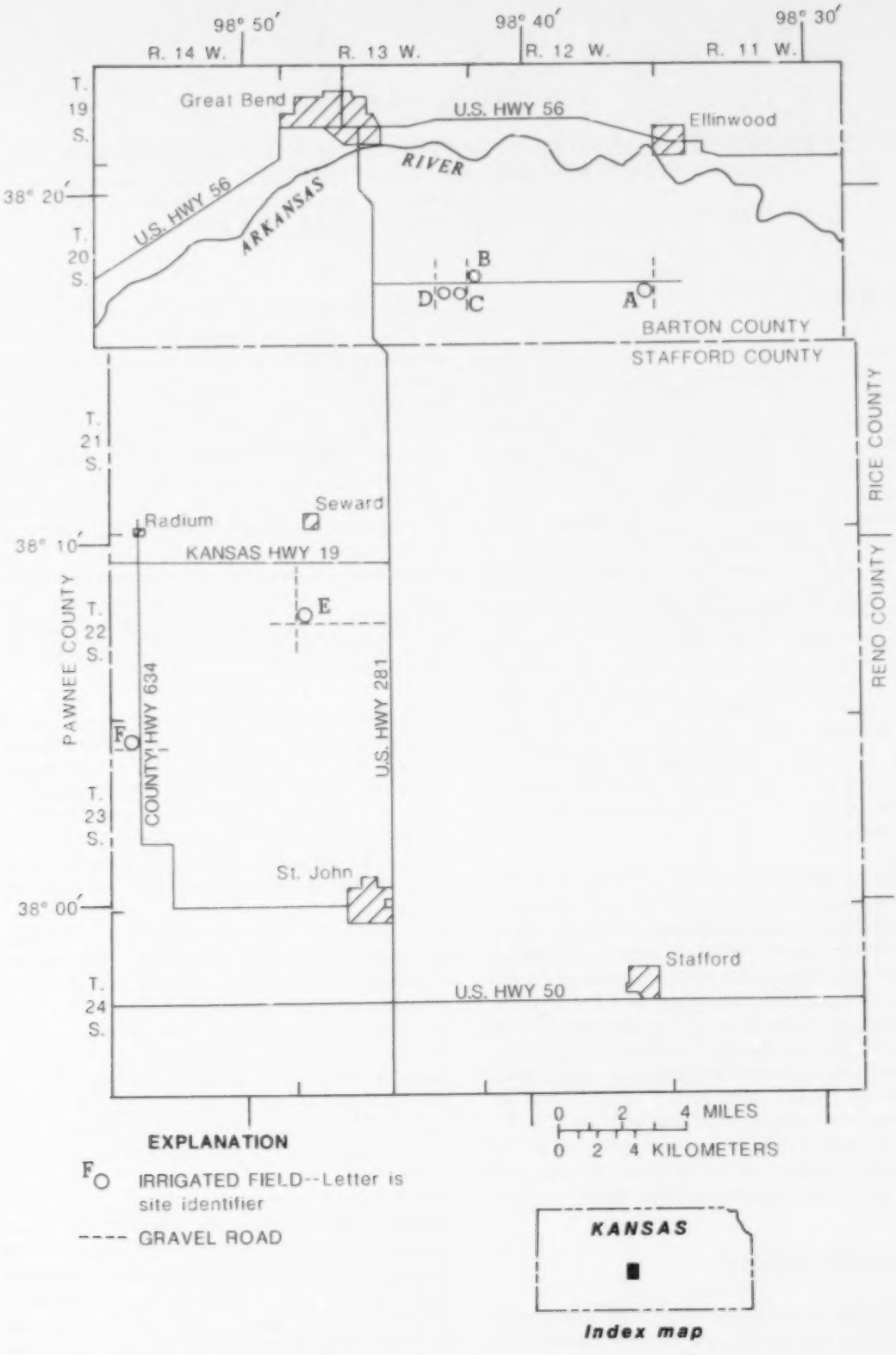


Figure 1. Location of study area and selected fields.

Access to irrigated fields with growing crops was essential to the success of this experiment. The U.S. Geological Survey acknowledges the cooperation of Sam Crissman, Jr., Ralph Phillips, Vernon DeWerff, and Charles Norris, landowners and operators who provided access to their fields and fertilizer- and pesticide-application records for this effort. Also, the Kansas Department of Health and Environment provided well-drilling equipment and drilling assistance at some of the study sites.

GROUND-WATER SAMPLING EXPERIMENT DESIGN

Six fields growing corn and irrigated by center-pivot sprinkler systems were selected as study sites, and the recent history of fertilizer and pesticide applications was obtained for each field. An observation well was installed and screened only in the top part of the aquifer in each field. Water from observation and irrigation wells was sampled for selected water-quality constituents, including nitrogen and atrazine which were applied to the fields. At one site (site E, fig. 1), where the water table was in an overlying sandy clay zone, a sample from the saturated sandy clay also was collected from a separate adjacent well and analyzed to determine if the water quality there was different from that of water in the underlying sand.

Description of Study Sites

Six fields were selected for this experiment based on the following criteria: (1) each field was planted to irrigated corn for at least the last 2 years; (2) the depth to water in the underlying aquifer was less than 40 ft, and (3) atrazine had been applied as a normal agricultural practice. These criteria are restrictive, and relatively few sites (including the six selected) were available that met all of them. Sequential years of growing one crop (corn) in a field is not common practice because of varying farm programs, economics, soil conditions, and changes in farm tenants. Depths to water of 20 ft or less were common in south-central Kansas when the last extensive water-level map was made in December 1973 (Fader and Stullken, 1978). Since that time, pumping for irrigation has mined the ground water, and depths to water that are 10 ft greater than those in 1973 are common. In addition, summer drawdowns from the pumped wells further depress water levels throughout the fields. The experiment was conducted in late summer, and depths to water were greater than 20 ft in each well.

The selected fields are shown in figure 1 and labeled as sites A-F. Maximum separation between fields is about 22 mi, and minimum separation is an adjacent quarter section (160 acres). The six sites have similar geohydrologic conditions; the aquifer is unconfined. All six fields overlie 90 ft or more of unconsolidated clay, sand, and gravel through which water flows to the east at a regional gradient of about 8 ft/mi (Stullken and others, 1987). Clay layers in the subsurface do not appear to be regionally extensive. However, a sandy clay zone immediately under the land surface seems to be very common and is 1 to 20 ft thick (Ralph Davis, Big Bend Groundwater Management District No. 5, oral commun., 1986). Bedrock throughout the area ranges from 90 to 210 ft deep.

Crop yields are enhanced by the consistent application of irrigation water, plant nutrients, and pesticides. The method and schedule of application can vary greatly depending on the season, soil characteristics, crop health, and personal philosophy of the grower. Typically, during preplanting the land is tilled and fertilized with gaseous anhydrous ammonia using tractor- or truck-mounted (ground-based) applicators. During the planting operation the corn row may be enriched further with an application of ammonium nitrate pellets. As the corn grows, more nitrogen may be applied along the sides of the row of corn. Finally, as the corn becomes too tall for ground equipment to pass without damaging the crop, liquid nitrogen is fed to the plant by mixing it with the center-pivot irrigation water (chemigation). Sandy top soil, such as that in south-central Kansas, usually requires frequent and small applications of nitrogen because of the tendency for the nitrogen compounds to leach below the root zone.

Herbicides, including atrazine, commonly are applied during the spring or early summer growing season with ground-based sprayers for preemergent control of broadleaf and grassy plants. When necessary, some herbicides may be mixed effectively and applied simultaneously

with the fertilizer. Herbicide applications are rarely made as the crop nears maturity.

Applications of nitrogen and herbicides at the study sites are summarized in table 1. Application quantities were obtained from each grower based on his records or recollection and probably vary in accuracy. The corn fields in the experiment were fertilized with 160 to 250 lb of nitrogen per acre.

In 1986, herbicides were applied to the study fields in late April as a preemergent weed control at the rates shown in table 1. Experience has helped each grower determine the level of concentration that is adequate for control, and the rates are often less than those recommended by the Kansas State Experiment Station guidelines (Nilson and others, 1986).

Description of Wells

The irrigation wells supplying water for the six selected fields pump water from screened intervals throughout the saturated zone. Wells often are not drilled to bedrock because sufficient water for irrigation is available within the middle part of the saturated thickness and because of a concern that pumping water from the deeper part of the aquifer may induce water of poorer quality to flow upward from bedrock formations.

It was planned that observation wells would be placed within each field of corn (that is, within the circle of chemical application) and only penetrate the upper 2 to 4 ft of the saturated zone. Distances from the irrigation wells ranged from 600 to 900 ft. During installation of the observation wells, it was found that the top few feet of saturated thickness was within the near-surface sandy clay zone. Small hydraulic conductivity and short penetration of the saturated zone made it difficult to obtain a sample. Therefore, the well screen was placed in the first sand zone below the sandy clay zone and water table. The sandy clay zones did yield enough water with time to attain static water levels equivalent to those in adjacent wells completed in the underlying sand.

Observation wells for this study consisted of 1.5- or 2-inch polyvinyl-chloride casing slotted near the bottom. The top of the casing was terminated about 20 inches below ground level to avoid conflicts with field-tillage equipment. The top of the casing was capped, and a metal disk placed over the top to aid in locating the well at a later time with a metal detector. The annulus of the bore hole was cemented to prevent vertical drainage from the surface. Lithologic logs, gamma logs, land-surface elevations, and water levels of the observation and irrigation wells in each field are given in figure 2.

Sample Collection

Samples were obtained once during August 1986 from each observation well by bailing because the water levels were too deep to pump samples with a surface-mounted pump. At least two casing volumes of water were removed from each well before sampling. Samples from the irrigation wells were obtained near the mouth of the pump while the crop was still being irrigated. Samples were prepared by standard methods and sent to the U.S. Geological Survey laboratory in Arvada, Colorado, for analysis of major inorganic ions, nitrite plus nitrate, and triazine herbicide. Onsite measurements of specific conductance, water temperature, pH, and alkalinity also were made for each sample.

Statistical Methods

Standard statistical techniques were applied to aid in the interpretation of the data for this experiment. The median sample concentration in water from the irrigation wells could be used to represent the quality of water that was withdrawn from a substantial part of the aquifer thickness. Also, the median sample concentration in water from the observation wells could be used to represent the quality of water from the upper part of the aquifer.

The difference between quality of water from the upper part of the aquifer and the integrated saturated thickness in the six fields is a subsample of the differences from all fields within the area. A range of median differences in constituent concentrations, or confidence interval, was determined based on the six sampled fields, and the true median difference of all fields is expected to be within this range.

Table 1. *Summary of nitrogen and herbicide applications*

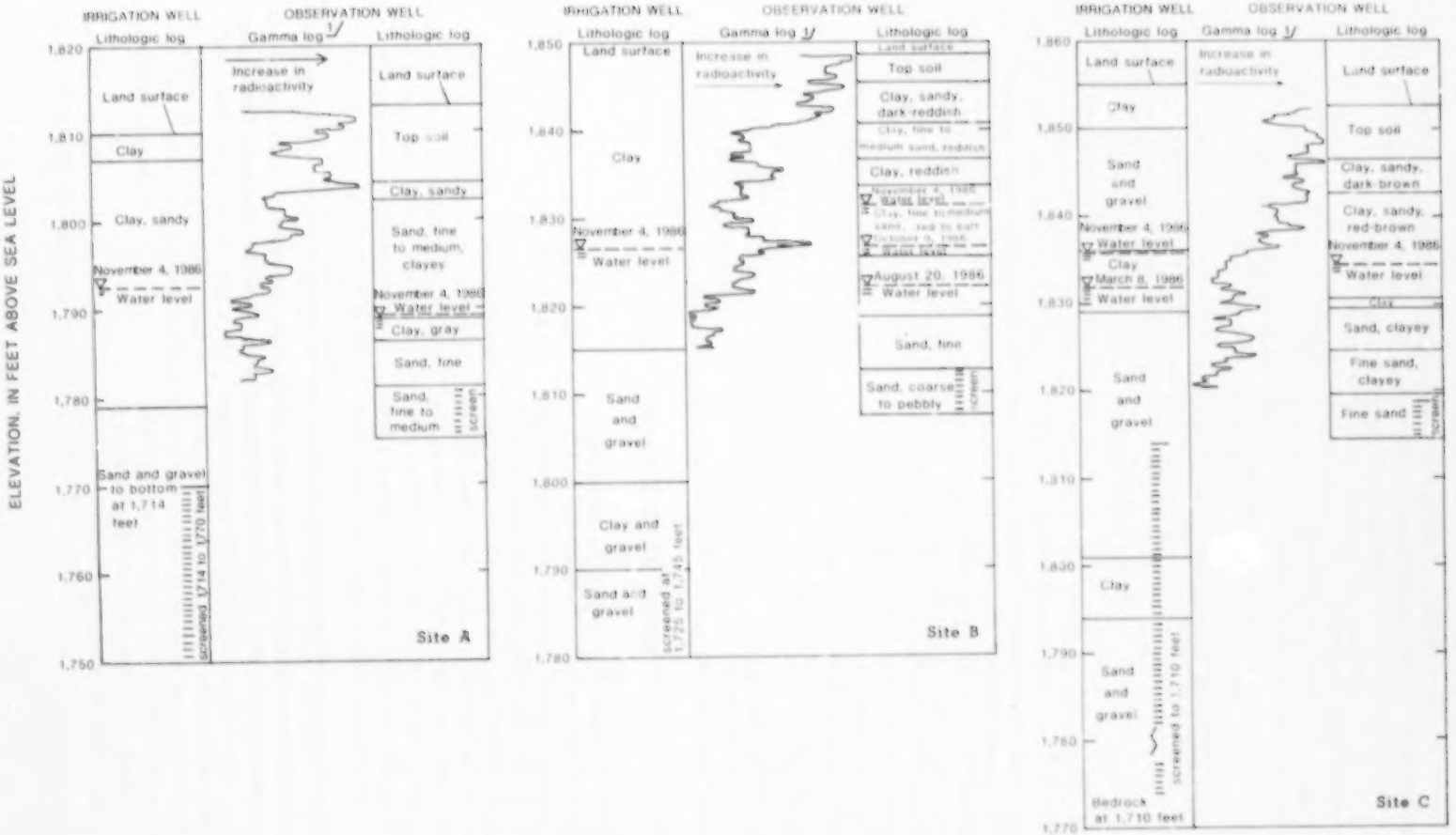
[The use of brand names (in parentheses) in this table is for identification purposes only and does not imply endorsement by the U.S. Geological Survey]

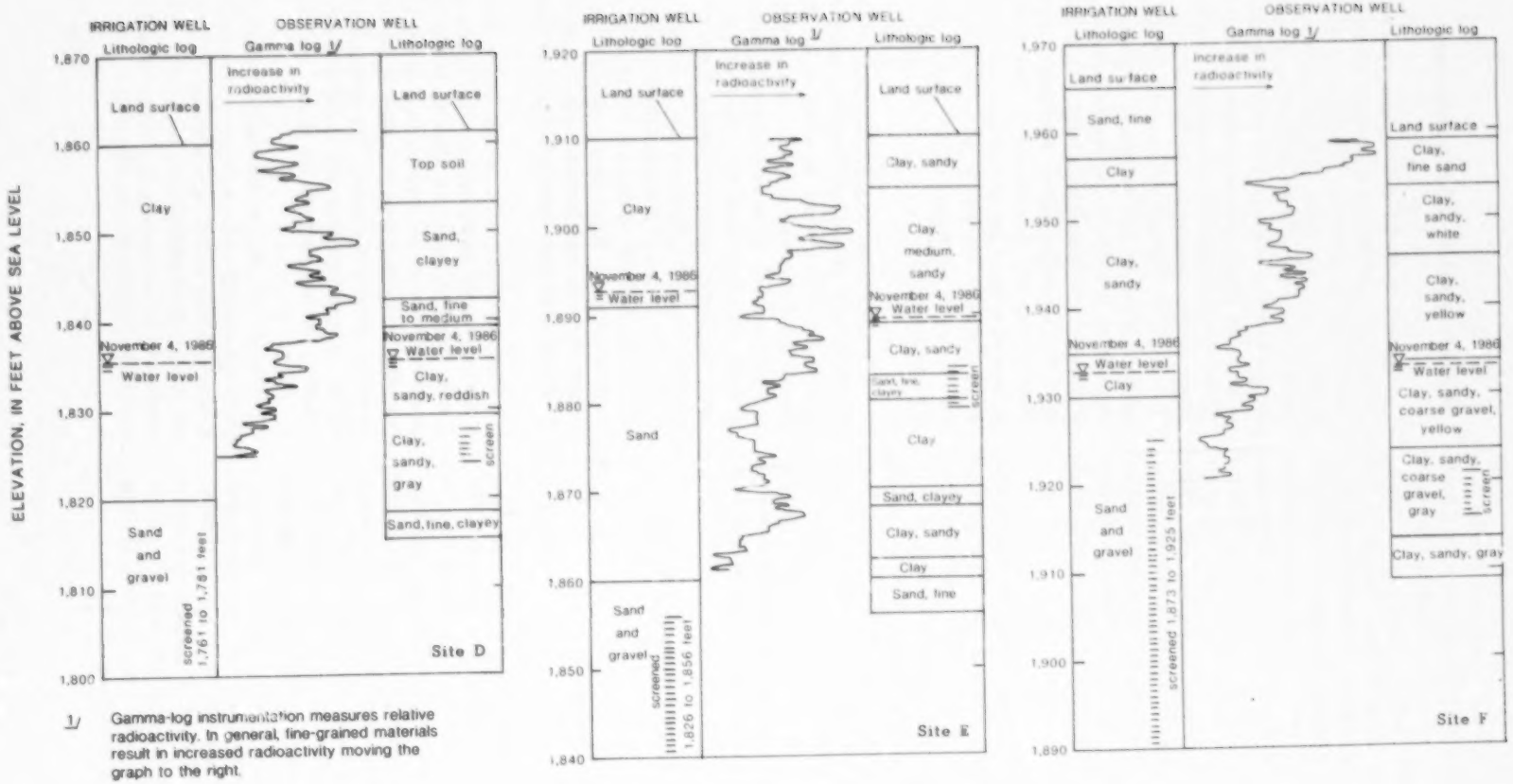
Study site and year (fig. 1)		Irrigation (inches)	Nitrogen (pounds per acre)	Herbicides (pints of active ingredient per acre)[1]					
				Atrazine (Aatrex)	Dicamba (Banvel)	Cyanazine (Bladex)	Metolachlor (Dual)	Alachlor (Lasso)	Propazine (Milogard)
A	1984	(2)	(2)	(2)	--	--	--	--	--
	1985	(2)	(2)	(2)	--	--	--	--	--
	1986	16	160	1	--	1	2	2	--
B	1984	(2)	(2)	(2)	--	--	--	--	--
	1985	(2)	(2)	(2)	--	--	--	--	--
	1986	16	160	1	--	--	--	2	--
C	1984	(2)	(2)	(2)	--	--	--	--	--
	1985	16	180	3.5	0.5	--	2	--	--
	1986	15	190	1	--	1	2	--	--
D	[3]1986	19	148	(2)	--	--	2	--	--
	1985	17	180	(2)	--	--	2	--	--
	1986	15	190	1	--	3	2	--	1.5
E	1984	18	250	1	--	--	--	4	--
	1985	18	250	1	--	--	--	4	--
	1986	18	250	1	--	--	--	4	--
F	1984	14	225	1	--	--	--	4	--
	1985	14	225	1	--	--	--	4	--
	1986	14	225	1	-	--	--	4	--

[1] Equivalent weight measure: Dual, 1 pound of active ingredient per pint, all others listed, 0.5 pound of active ingredient per pint.

[2] Application was made, but quantity is unknown (blanks, elsewhere in table, denote either no application or unknown quantity of application).

[3] Milo was grown instead of corn.


ELEVATION, IN FEET ABOVE SEA LEVEL
IRRIGATION WELL
OBSERVATION WELL
Lithologic log
Gamma log 1/
Lithologic log
Increase in radioactivity
Land surface
Clay
Clay, sandy
November 4, 1986
Water level
Sand and gravel to bottom at 1,714 feet
screened 1,714 to 1,770 feet
Top soil
Clay, sandy
Sand, fine to medium, clayey
November 4, 1986
Water level
Clay, gray
Sand, fine
Sand, fine to medium
screen
Site A
Clay and gravel
Sand and gravel
screened at 1,725 to 1,745 feet
Top soil
Clay, sandy, dark-reddish
Clay, reddish
August 20, 1986
Water level
Sand, fine
Sand, coarse to pebbly
Site B
Clay
Sand and gravel
Clay
Sand and gravel
screened to 1,710 feet
Bedrock at 1,710 feet
Clay, sandy, dark-brown
Clay, sandy, red-brown
March 6, 1986
Sand, clayey
Fine sand, clayey
Fine sand
Site C



1/ Gamma-log instrumentation measures relative radioactivity. In general, fine-grained materials result in increased radioactivity moving the graph to the right.

Figure 2. Lithologic and natural gamma-radiation logs, water levels, and screened intervals of wells.

An exact determination of the confidence interval of the median difference for all six fields was determined by a method described by Iman and Conover (1983), which uses binomial tables for small sample sizes of less than 20. The hypothesis that the median of the differences in constituent concentration (irrigation-well value minus observation-well value) was different from zero was tested at the 78- and 97-percent confidence levels. These specific confidence levels are those for which Iman and Conover (1983) provide binomial-table values. The sample concentrations in the extra sample (from the sandy clay zone at site E) were not used in the statistical analysis because the sample was collected only to compare with the sample from the underlying sand.

If the difference between sample medians fell within the confidence interval, the water quality in the irrigation wells (representing the integrated saturated thickness) was not considered significantly different from the water quality in the upper part of the saturated thickness of the aquifer. Conversely, if the difference was outside the confidence interval, the quality of water from the integrated saturated thickness was considered significantly different from the water in the upper part of the aquifer.

RESULTS OF GROUND-WATER SAMPLING

General Water-Quality Characteristics

Results of onsite measurements and chemical analysis are listed in table 2. The water sampled is a calcium bicarbonate type, is very hard (more than 200 milligrams per liter hardness), and has an alkalinity of about 200 mg/L (milligrams per liter). There also are large concentrations of sodium (about 40 mg/L). An increased sodium concentration is typical of a system of recirculated ground water. In this case irrigation water is applied causing seasonal saturation and desaturation of clay and soil layers that have a relatively large cation-exchange capacity. The pH of the ground water sampled is between 7.0 and 8.0, with a specific conductance of 250 to 1,150 µS/cm (microsiemens per centimeter at 25 °C).

Water-Quality Comparisons

Results of water-quality analyses are shown in figure 3, and results of statistical comparisons are shown in table 3. There is a significant difference in the nitrite-plus-nitrate concentrations at the 97-percent confidence level between samples taken from the irrigation wells and those from the observation wells. Nitrite-plus-nitrate concentrations varied from 5.2 to 16 mg/L in the observation wells and from 0.48 to 7.1 mg/L in the irrigation wells. The median concentration of nitrite plus nitrate was 3.4 mg/L in water from irrigation wells and 5.7 mg/L in water from observation wells. This difference is likely due to application of nitrogen fertilizers, which migrate downward to the top of the saturated zone. Also, the differences in hardness and alkalinity (larger in water from irrigation wells) were significant at the 97-percent confidence level.

The differences in concentrations of calcium, magnesium, and sodium (larger in samples from irrigation wells) were significant at the 78-percent confidence level but not at the 97-percent confidence level. Concentrations of sulfate and chloride in water from the observation wells were not significantly different from those in water from the irrigation wells at the tested confidence levels. Concentrations of atrazine were less than the detection limit of 0.1 µg/L (microgram per liter) in all wells except one irrigation well, which contained 0.1 µg/L. No other triazines were detected in any samples.

Comparisons of results from the two observation-well samples from the upper part of the saturated zone at site E show larger concentrations of all constituents in the sample from the sandy clay zone (E_c) than in the sample from the underlying sand. The concentration of nitrite plus nitrate was one order of magnitude larger in the sample from the sandy clay zone.

Results of this experiment demonstrate nonuniformity of some water-quality characteristics within the aquifer. Therefore, the interval of completion of a well must be considered in evaluating the representativeness of a sample collected from that well.

Table 2. *Compilation of water-quality characteristics*
[I, irrigation well; O, observation well]

Study site (fig. 1)	Date (August 1986)		Selected constituent concentrations or property values, in milligrams per liter, except as noted																			
			Laboratory measurements														Onsite measurements					
			Hardness, as $CaCO_3$		Calcium, dissolved as Ca		Magnesium, dissolved as Mg		Sodium, dissolved as Na		Sulfate dissolved as SO_4		Chloride, dissolved as Cl		Nitrite plus nitrate, dissolved as N		Atrazine (micrograms per liter)		Specific conductance (microsiemens per centimeter 25 degrees Celsius)		pH (standard unit)		Water temperature (degrees Celsius)		Alkalinity total as $CaCO_3$ (milligrams per liter)	
	I	O	I	O	I	O	I	O	I	O	I	O	I	O	I	O	I	O	I	O	I	O	I	O	I	O
A	12	19	210	450	75	150	6.4	18	51	41	29	24	84	120	6.0	16.0	<0.1	<0.1	680	1,130	8.0	[1]7.4	16	16	188	[1]193
B	12	19	240	260	83	92	7.5	7.5	41	39	32	38	63	50	1.3	5.5	< .1	< .1	656	725	7.1	7.4	16	17	217	236
C	8	19	230	150	80	53	7.3	4.6	44	35	43	32	51	4.3	1.5	5.8	< .1	< .1	631	454	7.2	7.5	15	16	217	176
D	8	19	190	210	63	72	7.7	7.1	49	33	29	39	51	37	.48	5.2	< .1	< .1	579	749	7.3	7.5	15	17	210	206
E	5	21	200	109	72	41	4.8	2.9	23	13	22	13	28	3.0	5.3	5.5	.1	< .1	470	256	6.9	7.5	16	16	185	120
E_c[2]	--	5	--	340	--	120	--	8.7	--	29	--	21	--	38	--	61	--	< .1	--	85	--	[1]7.6	--	22	--	136
F	7	27	180	64	62	21	5.8	2.9	23	69	22	22	15	14	7.1	7.9	< .1	< .1	544	447	7.2	7.5	15	14	170	154

[1] Laboratory measurement.

[2] Water from sandy clay zone at water table.

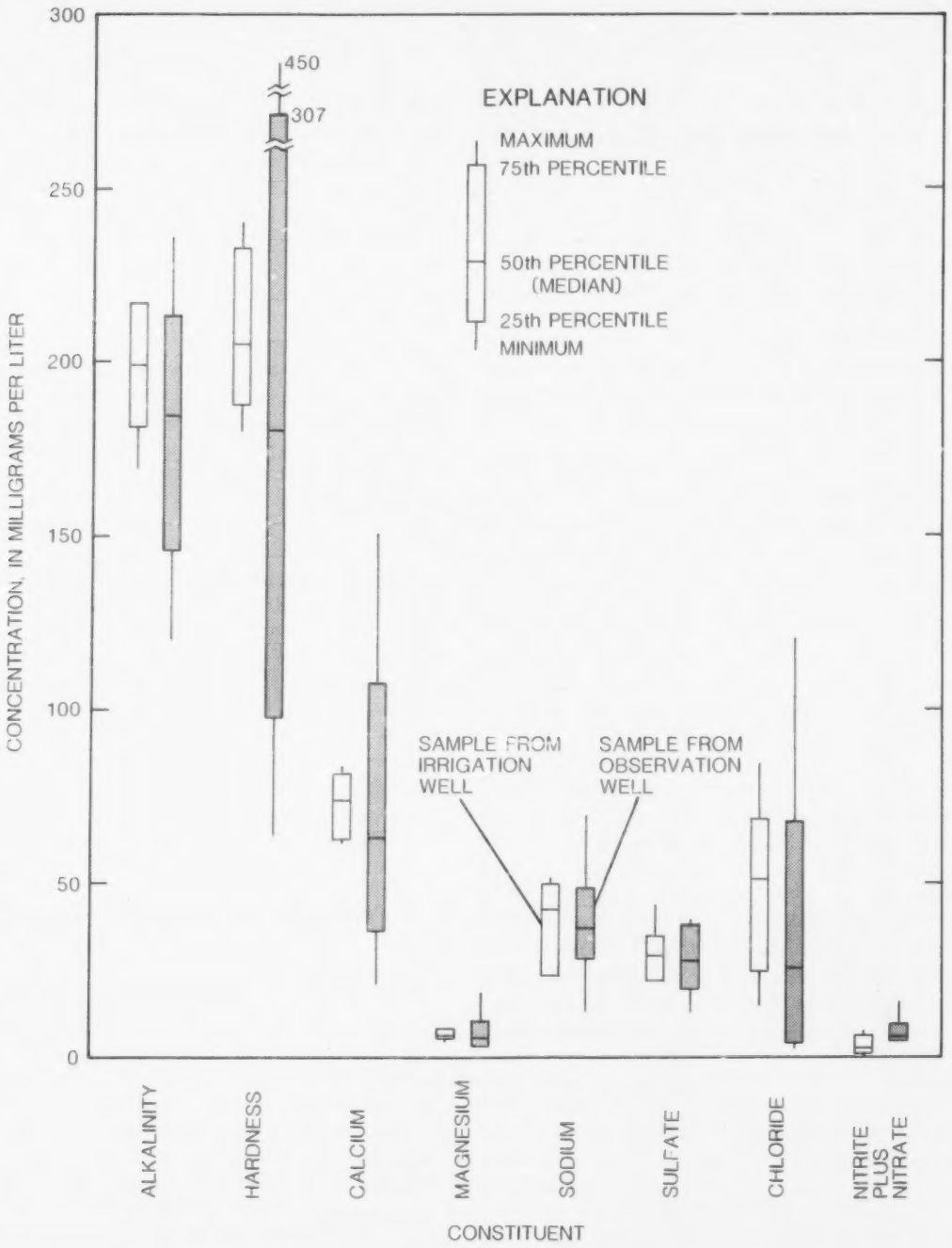
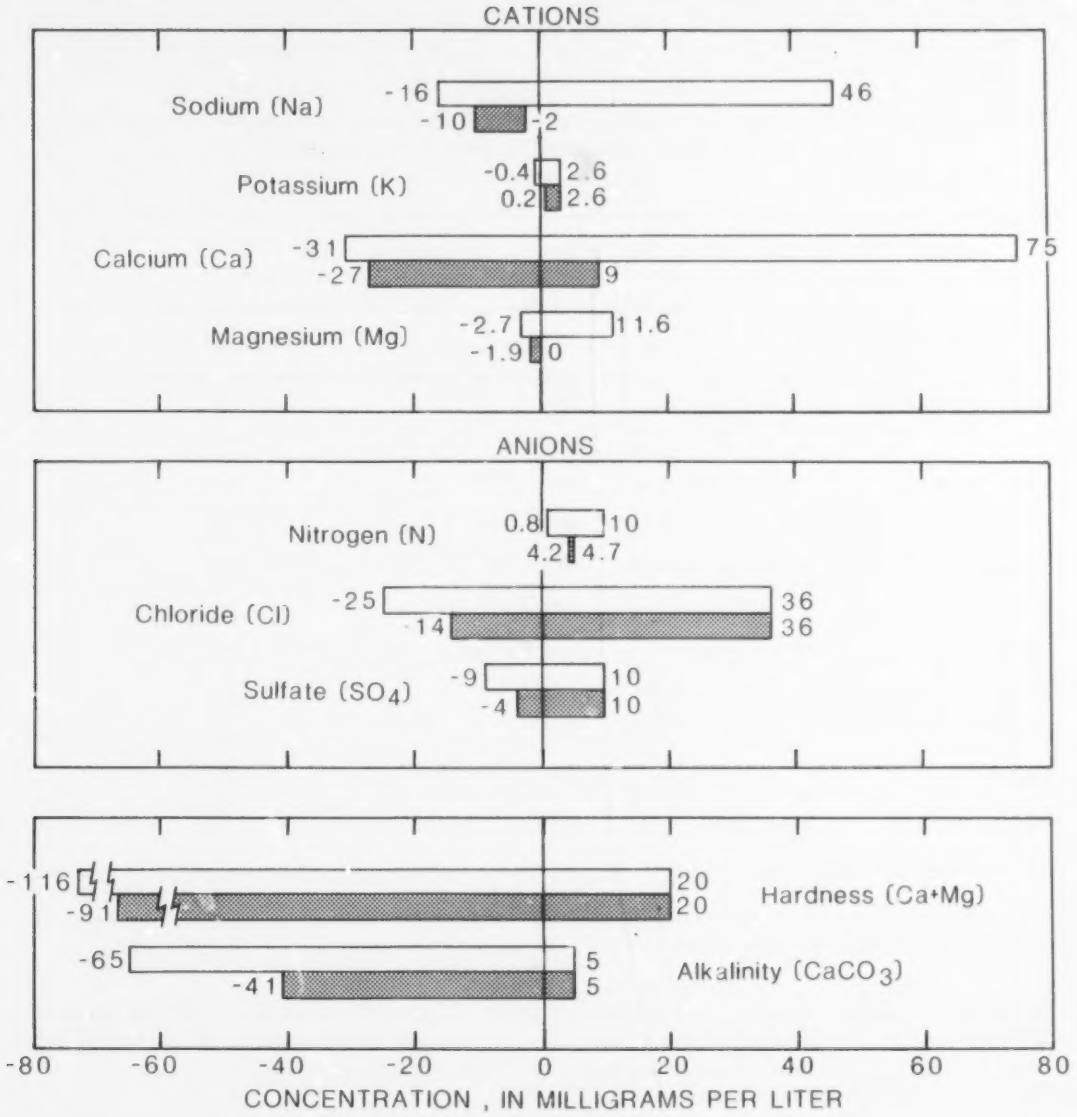


Figure 3. Concentrations of selected water-quality constituents.

CONCLUSIONS

Water-quality analyses indicated that larger concentrations of nitrite plus nitrate occur near the water table than deeper in the aquifer under the irrigated fields studied. This likely reflects the application of nitrogen fertilizer to the land. Concentrations of sulfate and chloride, constituents not applied to the land in the farming process, are similar in both shallow and deeper zones. Larger concentrations of calcium, magnesium, and sodium were found in water



EXPLANATION

WATER-QUALITY COMPARISONS

Top bar represents median difference in concentration at the 97-percent level. Bottom shaded bar represents median difference in concentration at the 78-percent level. Values at ends of bars indicate concentration difference at upper and lower confidence limit

Figure 4. Confidence limits of mean difference between sample concentrations from observation wells and sample concentrations from irrigation wells (irrigation-well median minus observation-well median), using a method described by Iman and Conover (1983).

Table 3. *Comparisons of concentrations or values of chemical constituents or properties between samples from observation wells and from irrigation wells*

Constituent or property	Statistically significant difference	
	78-percent confidence level	97-percent confidence level
Specific conductance	NO	NO
pH	YES	NO
Water temperature	NO	NO
Alkalinity	YES	YES
Hardness	YES	YES
Calcium	YES	YES
Magnesium	YES	NO
Sodium	YES	NO
Sulfate	NO	NO
Chloride	NO	NO
Nitrate plus nitrate	YES[1]	YES[1]

[1] Larger concentrations found in water from observation wells than in water from irrigation wells. In all other instances of significant differences, larger concentrations were found in water from irrigation wells.

from the irrigation wells. At site E, two samples from different zones in the upper part of the aquifer had concentrations of nitrite plus nitrate that differed by one order of magnitude.

It is apparent that, significant differences in some constituent concentrations in the observation wells as compared to concentrations in the irrigation wells indicate nonuniformity of some constituents within the aquifer. Water samples from partially penetrating wells or from individual wells may not necessarily represent the quality of water in the entire aquifer.

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